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(54) HEAT-RESISTANT RESISTOR PASTE AND HEAT-RESISTANT RESISTOR, ALONG WITH MANUFACTURE OF HEAT-RESISTANT RESISTOR

(57) Abstract

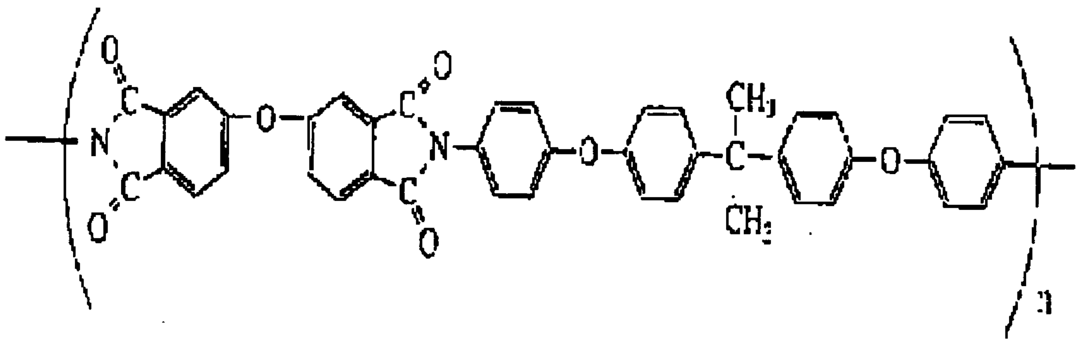
Problem

Heat-resistant resistor paste that can be used to make a resistor without a high heat treatment and having a good storage stability, a manufacturing process for a heat-resistant resistor involving the paste, and a heat-resistant resistor made with the paste in the method are provided.

Means for solution

Heat-resistant resistor paste containing both a binding-resin solution and a carbon-type conducting material is prepared. A solvent-soluble polyimide is used for the above-mentioned binding resin. A polyimide of Structure 1 is especially suitable.

Structure 1

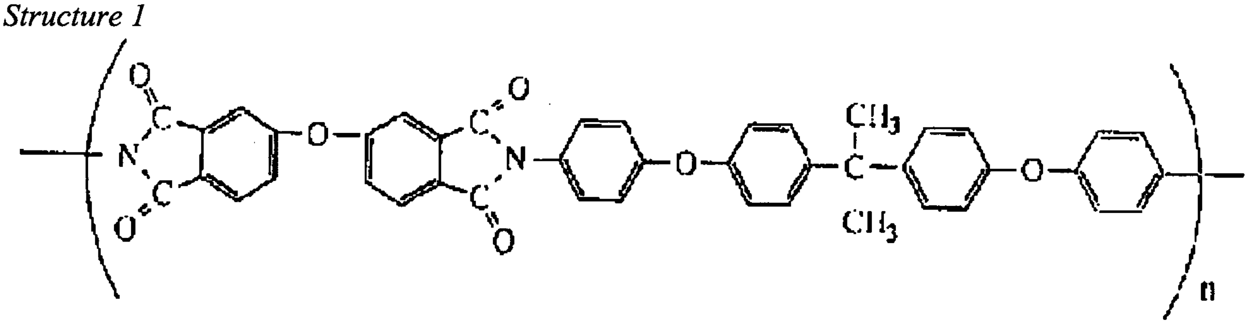


CLAIMS

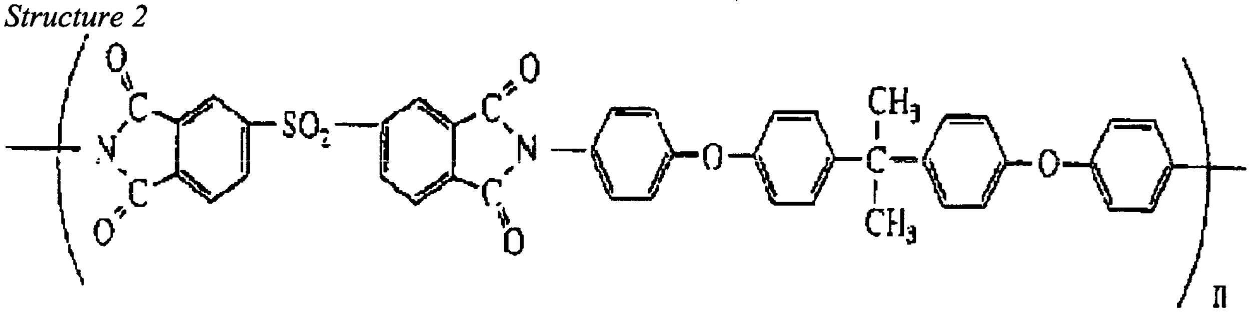
1. Heat-resistant resistor paste containing both a binding resin solution and carbon-type conducting material, characterized by the above-mentioned binding resin being a solvent-soluble polyimide.

2. The heat-resistant resistor paste described in Claim 1, and containing a polyimide of the following Structure 1 or 2:

Structure 1



Structure 2



3. The heat-resistant resistor paste described in Claim 1, and containing at least one type of carbon-type conducting material chosen from furnace black, acetylene black, channel black, graphite, and porous carbon.

4. The heat-resistant resistor paste described in Claim 1, and containing 100 parts by weight of binding resin solution and 30-60 parts by weight of a carbon-type conducting material.

5. The heat-resistant resistor paste described in Claim 1, and containing at least one type of non-conducting powder chosen from silica, alumina, glass, talc, clay, aluminum hydroxide, asbestos, titanium dioxide, and zinc oxide.

6. The heat-resistant resistor paste described in Claim 1, and containing at least one type of additive chosen from a defoaming agent, coupling agent, and disperser.

7. The heat-resistant resistor paste described in Claim 1, and involving a polar solvent.

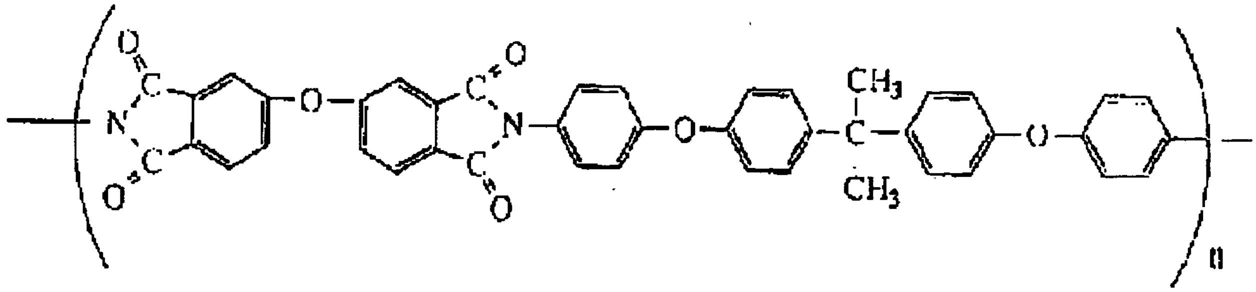
8. The heat-resistant resistor paste described in Claim 7, and involving at least one type of polar solvent chosen from N-methyl-2-pyrrolidone, N,N-dimethyl sulfoxide, N,N-dimethyl formamide, N,N-diethyl formamide, N,N-dimethyl acetamide, N,N-diethyl acetamide, and hexamethylene phosphoramide.

9. The heat-resistant resistor paste described in Claim 1, and containing 100 parts by weight of binding resin solution and 300-500 parts by weight of the solvent.

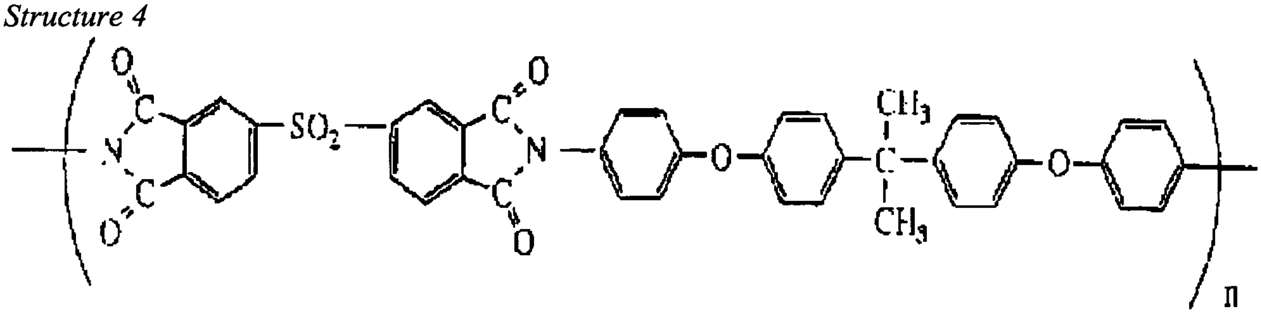
10. Manufacturing method for a heat-resistant resistor with the heat-resistant resistor paste described in Claims 1 through 9, involving heat-drying to remove the solvent.

11. Heat-resistant resistor containing both a carbon-type of conducting component and a binding resin component, which is a polyimide of Structure 3 or 4:

Structure 3



Structure 4



DETAILED EXPLANATION OF THE INVENTION

[0001]

TECHNICAL FIELD OF THE INVENTION

The present invention is concerned with both an electric resistor that can be used at a high temperature and a resistor paste used for manufacturing the electric resistor. It is especially concerned with both an electric resistor and a resistor paste containing a resin as a paste binding material.

[0002]

PRIOR ART

A resistor paste containing a resin as a binder was obtained by mixing a conducting powder with both a binding resin and a solvent. A powder of either conducting carbon black or graphite was used as a conducting powder to obtain the required resistance. A heat-setting resin such as phenol formaldehyde resin, xylene-modified phenol resin, epoxy resin, melamine resin, or acryl resin, or a polyimide precursor resin was used as the binding resin. The paste was used to make a resistor in a printing method.

[0003]

A resistor that is resistant at a high temperature is required for car sensors or for small electronic devices containing heating elements having a high calorific power. A resistor having good heat resistance had to be developed. Polyimide resins having good heat resistance have been used as binding resins for a resistor. Because the conventional type of polyimide resin is insoluble in solvents, the solvent-soluble polyimide precursor resins have been used as binding resins for a paste (Japanese Kokai Patent Application Hei 8[1996]-81628).

[0004]

PROBLEMS TO BE SOLVED BY THE INVENTION

The conventional type of heat-resistant paste containing a solvent-soluble polyimide precursor resin as the conventional type of binding material had to be made by the condensation imidation of the amic acid contained in the polyimide precursor resin in a heat-treatment process at 250-300°C to convert the binding resin to a heat-resistant polyimide resin. The high-heat treatment caused an energy-cost increase or a global environmental problem. Any part, such as a substrate, that was heat treated with a resistor had to be made with a material having a good heat resistance, causing a cost increase.

[0005]

Because the condensation and imidation of a polyimide precursor resin was gradually carried out at standard temperature in the form of a stable storage paste, the solubility in solvents was reduced, the viscosity of the paste was increased, and gelling occurred. The properties, including the printing property, of the paste that were required for resistor formation were reduced. Because an additive used to prevent gelling had to be used for the conventional type of heat-resistant resistor paste containing a polyimide precursor resin used as a binding material, or because the paste had to be refrigerated, the conventional type of paste was expensive.

[0006]

The present invention solves the above-mentioned problems of conventional products. A resistor can be made without a high-heat treatment. The present invention provides both a heat-resistant resistor paste having a good storage stability and a heat-resistant resistor containing the paste.

[0007]

MEANS TO SOLVE THE PROBLEMS

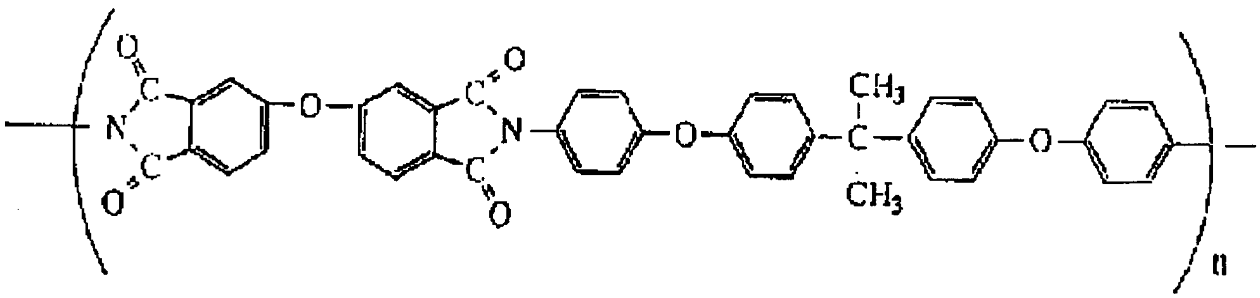
The heat-resistant resistor paste of the present invention contains both a binding resin solution and a carbon type of conducting material, and is characterized by containing the above-mentioned binding resin, which is a solvent-soluble polyimide.

[0008]

The above-mentioned heat-resistant resistor paste suitably contains a polyimide of the following Structure 5 or 6.

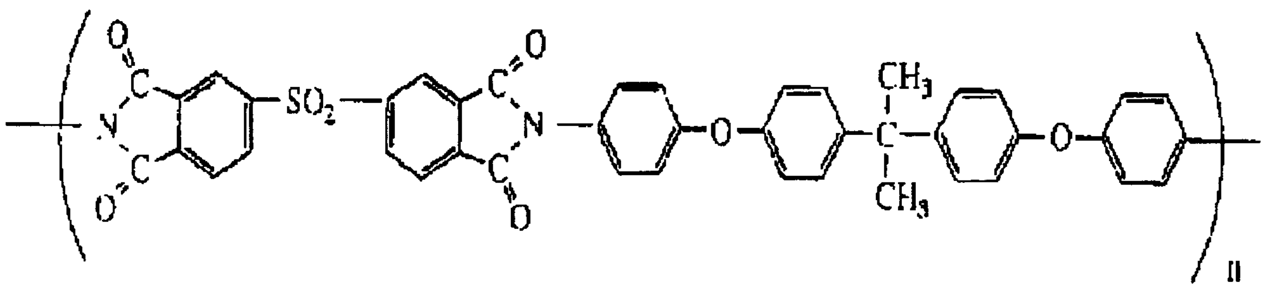
[0009]

Structure 5



[0010]

Structure 6



[0011]

The heat-resistant resistor paste suitably contains at least one form of carbon-type conducting material chosen from furnace black, acetylene black, channel black, graphite, and porous carbon.

[0012]

The heat-resistant resistor paste suitably contains at least one type of non-conducting powder chosen from silica, alumina, glass, talc, clay, aluminum hydroxide, asbesto, titanium dioxide, and zinc oxide.

[0013]

The heat-resistant resistor paste suitably contains 100 parts by weight of binding resin solution and 30-60 parts by weight of a carbon-type conducting material, and contains at least one type of additive chosen from a deforming agent, coupling agent, and disperser.

[0014]

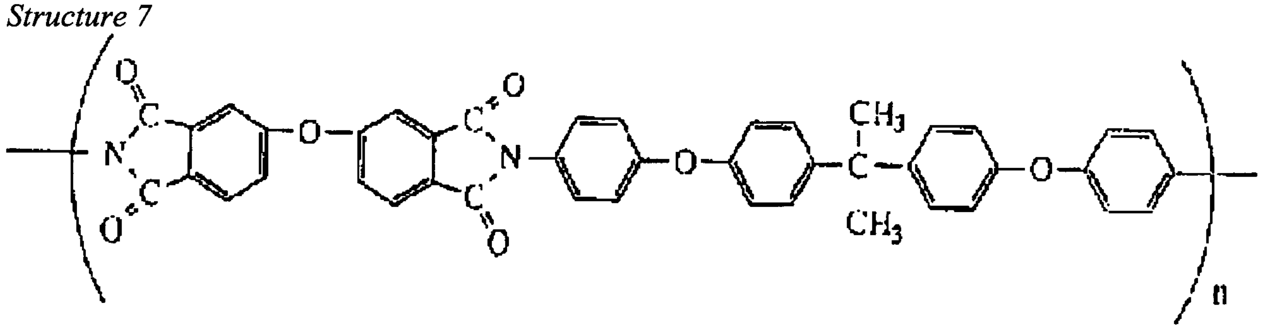
The heat-resistant resistor paste suitably involves at least one type of polar solvent chosen from N-methyl-2-pyrrolidone, N,N-dimethyl sulfoxide, N,N-dimethyl formamide, N,N-diethyl formamide, N,N-dimethyl acetamide, N,N-diethyl acetamide, and hexamethylene phosphoramide.

[0015]

The manufacturing method for the heat-resistant resistor of the present invention is characterized by involving a heat-resistant resistor paste containing both a solvent-soluble polyimide solution and a carbon-type conducting material. The heat-resistant resistor of the present invention is characterized by containing both a carbon-type conducting component and a binding resin component, which is a polyimide of Structure 7 or 8.

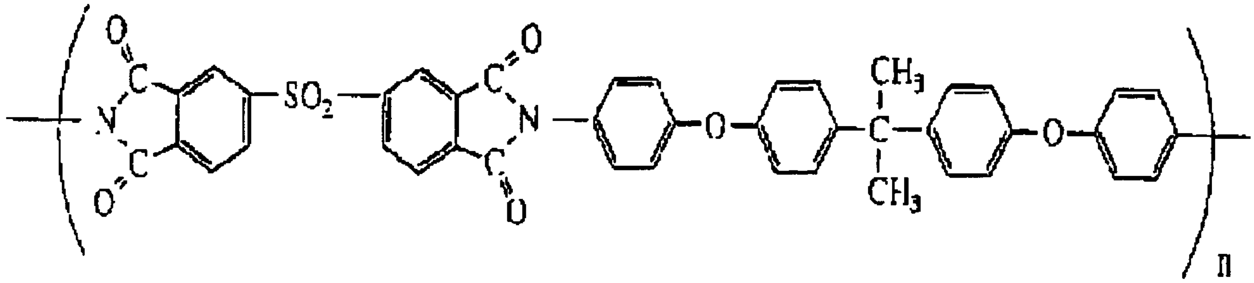
[0016]

Structure 7



[0017]

Structure 8



[0018]

APPLICATION OF THE PRESENT INVENTION

Because the heat-resistant paste of the present invention contains a binding resin, which is not a polyimide precursor resin but a solvent-soluble polyimide resin, it requires no heat treatment at 250-300°C for the condensation imidation of the amic acid contained in the polyimide precursor resin in the resistor manufacturing process. After printing, it may be heated under suitable conditions to remove the solvent.

[0019]

Problems of the conventional type of heat-resistant resistor paste containing a polyimide precursor resin as a binding material, including the energy-cost increase for resistor manufacture, and global environmental problems caused by the energy use, as well as the requirement of a material having a good heat resistance for any part, such as a substrate, heat-treated with a resistor, can be solved by the present invention.

[0020]

Because a polyimide is contained as a binding resin in a storage-stable paste, no condensation imidation is gradually carried out at standard temperature, while condensation and imidation of the conventional type of paste containing a polyimide precursor resin type of binding material is carried out gradually at standard temperature. The viscosity of the paste is not increased and gelling does not occur. No properties required for manufacturing a resistor, including the printing property of the paste, are reduced. Neither an additive used to prevent gelling nor refrigeration is required. The present invention reduces the cost significantly.

[0021]

The heat-resistant resistor paste of the present invention is characterized by containing a polyimide of the above-mentioned Structure 5 or 6. Because there are relatively large amounts of

the sp^3 type of chemical bonds, such as ether bonds, between the aromatic components in the molecule, the majority of molecules are non-linear. Because the molecules are hardly coagulated in the solvent due to the structure, the polyimide is easily dissolved in the solvent. Because the heat-resistant resistor paste of the above-mentioned Structure 6, described in the present invention, contains sulfone bonds in the molecule, the solubility is significantly improved.

[0022]

A heat-resistant resistor paste having a high solid density is obtained in the application of the present invention. Because a thick film is obtained per paste printing, the printing number is significantly reduced in the resistor manufacturing process, and the cost is significantly reduced. Because the viscosity of the paste is increased in the low shearing-rate region, the amount of paste that drips in the printing process is reduced. The heat-resistant resistor paste of the above-mentioned Structure 7 or 8, described in the present invention, is more effective than the above-mentioned paste.

[0023]

Examples of the carbon-type conducting powder used in the present invention include furnace black, acetylene black, channel black, graphite, and porous carbon. It is suitable to use 100 parts by weight of the binder resin and 30-60 parts by weight of a carbon type of conducting material.

[0024]

The heat-resistant resistor paste of the present invention may contain a non-conducting material such as silica, alumina, glass, talc, clay, aluminum hydroxide, asbestos, titanium dioxide, or zinc oxide. It is suitable to use 100 parts by weight of the binder resin and 5-50 parts by weight of a non-conducting material. It is especially suitable to use a total resin and non-conducting material amount that is close to the amount of resin alone.

[0025]

The heat-resistant resistor paste and heat-resistant resistor of the present invention may contain additives such as a deforming agent, coupling agent, or disperser. It is suitable to used 100 parts by weight of binder resin and 1-3 parts by weight of disperser.

[0026]

One or more types of polar solvent, including N-methyl-2-pyrrolidone, N,N-dimethyl sulfoxide, N,N-dimethyl formamide, N,N-diethyl formamide, N,N-dimethyl acetamide, N,N-

diethyl acetamide, and hexamethylene phosphoramide, may be contained in the present invention. It is suitably used at 300-500 parts by weight with 100 parts by weight of the binding resin.

[0027]

APPLICATION EXAMPLES

In the following, the details of the present invention are explained with application examples.

APPLICATION EXAMPLE 1

The solubility of the polyimide of the present invention in a solvent was evaluated. An N-methyl-2-pyrrolidone solvent used for screen ink containing the conventional type of polyimide precursor was used. In the case of a polyimide of the above-mentioned Structure 5 (referred to as polyimide A below), it was effective in obtaining a paste with a maximum density of 20 wt% [sic]. In the case of a polyimide of the above-mentioned Structure 6 (referred to as polyimide B below), it was effective in obtaining a paste with a maximum density of 32 wt%.

[0028]

It was assumed that polyimide B was more soluble than polyimide A because polyimide B contained sulfone bonds in the molecule. Because the polyimide precursor resin used for the conventional type of resistor paste was effective in obtaining a paste with maximum density of 20 wt%, the solubility of the polyimide of the present invention was as good as that of the conventional type of polyimide precursor resin.

[0029]

APPLICATION EXAMPLE 2

The following ingredients were mixed together, kneaded, and dispersed by a 3-roll mill to obtain a resistor paste.

Binding resin (solid)	100 parts by weight
Carbon black (made by Denka Kogyo, acetylene black)	50 parts by weight
N-methyl-2-pyrrolidone solvent	400 parts by weight

Both Polyimide A and B were used as a binding resin. A specific type containing a polyimide precursor compound (made by Ube Kosan) used for the conventional type of resistor paste was evaluated in the comparative example.

[0030]

Each resistor paste was sealed and left undisturbed at 23°C. The variation of the paste viscosity corresponding to the [storage] time was evaluated. A conical rotary type of viscometer (rotator size: 25 mm, conical angle: 0.1 radian, shearing rate: 10 1/s [sic]) was used for the viscosity measurement. Polyimide A: viscosity/primary viscosity = 1.01, Polyimide B: 1.02, polyimide precursor (conventional type): 2.10 after leaving it undisturbed for 6 months

[0031]

In the case of a paste containing a polyimide, a smaller increase in the viscosity resulted than in the case of a paste containing a polyimide precursor compound, and a good paste pot life was obtained.

[0032]

APPLICATION EXAMPLE 3

Each resistor paste obtained in Application Example 2 was used for screen-printing with a screen (200 mesh) on a polyimide film and dried at 120°C for 10 minutes. A resistor film was obtained. A film thickness of 10±1 μm was obtained by controlling the other printing conditions.

[0033]

A paste containing a polyimide precursor was used to make a sample in the above-mentioned process. Another sample made in the above-mentioned process, followed by the sintering process after the drying (conventional sample), was also used.

[0034]

The surface-area resistance of each sample resistor was measured. The variation of the resistance of each sample resistor over time was evaluated after leaving it undisturbed at a high temperature (150°C-500 hours) and at high humidity (80°C-90%RH-500 hours). Table 1 shows both the surface-area resistance and resistance/primary resistance (percentage).

[0035]

Table 1

Evaluation items / Binding material resin	Primary surface-area resistance (kΩ/□)	Variation of resistance after 5000 hours (%)	
		At high temperature	At high humidity
Polyimide A	4.58	-1.50	-0.13
Polyimide B	4.21	-2.00	-0.21
Polyimide precursor (sintering process)	4.70	-2.50	1.02
Polyimide precursor (no sintering process)	5.15	-52.01	-27.03

[0036]

In the case of either a resistor containing a polyimide as a binding material resin and obtained by sintering, or containing a polyimide precursor compound as a binding material resin and obtained by sintering, a resistance variation of 5% or less was obtained at a high temperature and at high humidity. Either paste could be used. In the case of a resistor containing a polyimide precursor and obtained by not sintering, a resistance of –52% (high temperature) and of –27% (high humidity) were obtained. The resistor could not be used. In the case of a resistor paste containing a polyimide precursor resin binder, condensation imidation of the polyimide precursor binder could not be completed at 120°C for 10 minutes. While the resistor was left undisturbed at a high temperature, condensation imidation of the binder resin was carried out, resulting in contraction of the binding resin component and in a reduction of the resistor resistance.

[0037]

APPLICATION EXAMPLE 4

The creep limit of each resistor obtained in Application Example 3 except for a resistor containing a polyimide precursor compound as a binding material resin and obtained by not sintering (poor stabilization of resistance) was evaluated. Each resistor was fixed to an actual variable resistor; the variable resistor was operated once (both ways), and abrasion of each resistor was measured for the evaluation. Six resistors containing alloys of Pd, Ag, Pt, Cu, Zn, and Ni were used. This made contact with a resistor with a 10-g load, thickness of 0.3 mm, and width of 0.5 mm. Abrasion was measured by a contact type of surface roughness meter. Table 2 shows the results.

[0038]

Table 2

Binding material resin	Resistor abrasion (μm)
Polyimide A	0.3
Polyimide B	0.4
Polyimide precursor (sintering process)	0.3

[0039]

The abrasion resistance of the resistor containing a polyimide described in the above-mentioned application examples was equal to that of a resistor containing the conventional type of polyimide precursor, so it can be used.

[0040]

EFFECTS OF THE INVENTION

A resistor can be made without a high-heat treatment in the present invention. A heat-resistant resistor paste that is stable with respect to storage, a manufacturing method for a heat-resistant resistor involving the paste, and a heat-resistant resistor obtained with the paste are provided by the present invention.

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